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Influence of Polymer Melt Behavior on Flammability

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Abstract

As the initial step in a study of the role of polymer melt viscosity in polymer burning behavior, a simpler, non-burning configuration has been examined. Vertical slabs of two types of polypropylene have been subjected to uniform radiative heating on one face. The subsequent melt flow process was monitored by measuring weights, temperatures and flow velocities. A low MW polypropylene flowed freely at temperatures below those for significant degradation whereas a commercial polypropylene of higher MW degraded and gasified extensively. Plans are described for modeling the non-reactive case first.

Introduction. In certain consumer product areas, such as electronic devices and automobiles, complex molded parts made from thermoplastic polymers are increasingly common. Low part costs for large production runs and the ability to integrate into one piece what formerly required several individual parts make this a trend which is likely to continue. The commodity polymers, such as polypropylene and polystyrene, which are used for these components are inherently flammable unless properly treated with flame retardants. However, as noted by Kashiwagi [1] in another paper presented here, there is a shift occurring in the nature of acceptable flame retardants for ecological reasons. These two trends, the growth in thermoplastic components and the shift in the nature of flame retardants, provide an incentive to look at the flammability behavior of thermoplastics and to assess the extent to which this behavior may affect the appropriate choice of new means of flame retardancy. This paper is a progress report on a study of these issues.

Experience with the burning of thermoplastic automotive components has demonstrated that it is a very complex process dependent on several factors. The central complexity, long recognized, is that thermoplastics inevitably change shape as they are subjected to the heat of the burning process. This is probably the chief reason why the literature contains few results in this area [2, 3]. Time-dependent changes in fuel geometry make modeling of the burning process much more challenging.

Shape change is typically accompanied by the movement of hot, lowered viscosity material to some new location under the influence of gravity. This polymer "melt" may be burning, both as it moves and in its new location. Thus the growing fire on the part re-shapes it, moving heated material and this, in turn, alters the fire growth process. The net result can depend strongly on where the moving material comes to rest and on the thermal properties of the material on which it

rests. Thus, for example, the polymer melt can form a burning pool near the original part location so that the flames from this pool interact with this burning part or, in the opposite extreme, the melt can fall a substantial distance and be quenched on a cold, heat absorbing surface, thus robbing the original fire of fuel. The heat release rate of such a thermoplastic part can thus vary strongly with the physical circumstances in which it is burned.

The above behavior is not seen when testing horizontal samples of material in the Cone Calorimeter. When one is assessing new flame retardant materials for thermoplastics, it is desirable to also look at them in modes that resemble their likely real world behavior.

As a first step along the above lines, NIST has initiated a study of polymer melt behavior in a very simple configuration: a thick, vertically oriented slab. Before examining the burning process itself, we are looking at an idealized version of it to see if this can be modeled. Thus this slab of thermoplastic is subjected to spatially uniform radiative heating on one surface.

Description of Experiments. Figure 1 is a sketch of the polymer heating experimental apparatus. A panel heated by the burning of natural gas uniformly irradiated the front face of a polymer sample (5.7 cm wide by 25 cm high by 25 mm thick). The sample was insulated on its lateral edges and its back surface; its weight was measured by a scale which supported the sample frame. This scale had a resolution of 1 g. Polymer melt material was captured by a pan atop a second scale after a free drop of about 30 cm. This scale had a resolution of 0.1 g. The temperature of both scales was monitored to assure that they did not heat significantly.

In separate experiments the radiant flux to the polymer samples was varied. The intent was to hold this flux constant during the exposure (which began with the removal of a water-cooled shutter). However, the panel showed an initial spike in its flux of 25 % or more above the test-average flux (apparently because of variation in the rate of radiative losses from the panel in the presence vs absence of the shutter). The transient behavior of the flux was followed by a flux gage placed next to the sample; the initial spike decayed after about 2 min to 3 min. The time-average radiant flux (which is the value reported below) was varied from the lowest level at which the panel remained reasonably stable (ca. 8 kW/m^2) to flux levels somewhat less than those seen in wall flames (maximum here of 26 kW/m^2). The flux gage was calibrated against a standard and should have an uncertainty within ± 5 %. The exposure time was varied from 10 min at the highest fluxes to 45 min at the lowest.

At intervals during a test, a mechanically-supported thermocouple (0.05 cm dia. sheath; chromel/alumel) was inserted nearly tangentially into the outer portion of the surface melt layer to get a measure of this surface temperature. This was done at two heights on the vertical centerline of the sample, usually about 5 cm from the top and 5 cm from the bottom. There were small systematic differences between the measurements at the two heights which have not yet been analyzed; the average is reported here. The temperature readings from this thermocouple varied with its exact placement (affecting the extent of lead wire wetting by the melt); the values reported are the maxima. There is insufficient information to assess the absolute accuracy of this result as a measure of melt surface temperature. A single thermocouple was placed at the back of

the sample (near its center) at its interface with the 25 mm block of ceramic fiber insulation there. A single thermocouple (bare junction made from 0.013 cm dia. chromel/alumel wire) was also placed in the melt pool, just above the catch surface, near the point at which melt material flowed in.

Small flakes of thin Kapton[1] polyamide (0.013 mm thick; typically ca. 3 mm square) were placed onto the upper region of the melt surface at intervals to serve as a means for estimating the downward flow velocity of the outer surface of the melt. The behavior of these was recorded by a Hi-8 video camera. The data have not yet been analyzed but preliminary tests gave velocities on the order of 1 cm/s.

Preliminary tests were performed with commercial grades of low density polyethylene, high density polyethylene and polypropylene. The two polyethylenes exhibited a skin-forming behavior during heat-up which rendered their subsequent melt flow erratic and very complex. Thus the work reported here has focused on polypropylene which shows only some yellowing during heat-up. The results below compare the behavior of a commercial polypropylene (here denoted as PP) and a low molecular weight polypropylene having a weight mean molecular weight of 23,000 (here denoted as 23kPP).

The melt viscosity of the polymer as a function of temperature is a key determinant of its behavior in these experiments (and during burning). A rheometer was used to obtain preliminary measures of viscosity as a function of temperature and shear rate.

Experimental Results and Discussion. Figure 2 shows the approximate steady-state mass loss rate from the two types of polypropylene as a function of the incident radiant heat flux. (The mass loss behavior was nearly steady for these tests but the values shown are those from late in each test where the loss rate was a maximum.) The commercial material was barely hot enough to begin to lose mass in a 45 min exposure at 8 kW/m^2; as the incident flux was increased, the mass loss rate became substantial. The 23kPP, on the other hand flowed freely, even at the lowest heat flux; this loss rate increased almost linearly with an increase in the flux. Curves for both materials imply that the loss rate would be still greater if the heat flux were increased to the level (30 kW/m^2 to 40 kW/m^2) provided by flames on a vertical surface at this scale.

Rheometric measurements on these materials are in need of further study but they show a substantial shear rate dependence, indicative of non-Newtonian behavior. The zero shear viscosity of the commercial PP is, of course, much higher than that of the 23kPP. The difference is so large that measurements could not be made in overlapping temperature ranges. Thus the 23kPP shows an apparent viscosity which decays to small values (few Pa-s) by ca. 175 °C; the

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[1] Certain trade names and company products are mentioned in the text in order to specify adequately the equipment used. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the products are necessarily the best available for the purpose.

commercial PP reaches comparable viscosity values only well above 250 °C (measurements have yet to be made above this temperature). All measurements thus far have been in air; nitrogen may give different behavior due to lack of oxidative interactions which can alter the molecular weight and thus the melt viscosity. It is not feasible to measure viscosity at high temperatures, comparable to those reported below for the surface temperature of the commercial PP.

Figure 3 shows the average surface temperatures for the two materials in the same incident heat flux range. Note that at equal heat fluxes the surface temperature of the 23kPP was as much as 200 °C less than that of the commercial PP. At the same time its mass loss rate was roughly twice as high. This was simply a result of the low melt viscosity of the 23kPP. Nearly all of the net absorbed heat was being carried away as the sensible heat content of the polymer melt. Figure 4 shows that virtually all of the mass lost from the 23kPP ended up in the melt pool. Note that there is no indication that fire level heat fluxes would change this. Note also that the data for this material imply that it would be difficult to make it burn in this vertical configuration because it tends to "melt" away at a temperature too low to provide any gas phase fuel.

Figure 4 also shows that slightly less than half of the commercial polypropylene ended up in the melt pool. The remainder had been vaporized. Rather surprisingly, the fraction vaporized did not change appreciably as a function of heat flux even though Figure 3 shows that the surface temperature was varying by about 150 °C over the flux range examined here (recall also the exposure time varies from 10 min to 45 min, inversely with the heat flux). Some further tests are planned to check the apparent constancy of the fraction vaporized in light of the small mass losses at the low flux end. Figure 4 implies that during burning about half of the commercial PP would feed a flame on the face of the sample and half would flow away to burn in a melt pool. Burning experiments are planned to check these inferences.

From a modeling standpoint, the 23kPP appears simpler. The data here suggest that this experiment could be modeled without the inclusion of any degradation chemistry. The commercial PP, on the other hand, degraded extensively in these tests. Viscosity measurements on material from its melt pool gave values much lower than on the starting material, implying a substantial decrease in molecular weight. This could be the result of both pyrolytic and oxidative reactions in the present set-up where air had free access to the hot surface.

Model Description. Polymer melt behavior is very complex; even the simple two-dimensional configuration studied here poses a challenge to the modeler. The most basic description must include equations of mass, momentum, and energy, with flow driven by gravity and temperature rise dictated by an imposed heat flux. The geometry of the problem changes considerably with time. The surface of the melt is a free surface that may undergo considerable deformation, and the internal interface between the solid and melted polymer moves through the material as it heats. The flow is in large part determined by wide variations in viscosity, whose strong dependence on both temperature and molecular weight should ultimately be included in the model. If the temperature increase is high enough, the polymer begins to gasify, and chemical reactions must be taken into account in calculations of heat and mass transport. The material properties of the vertical holder also affect the heat transport.

This complex problem can be modeled using the capability of the commercial finite-element program FIDAP. This software provides the means to model flow processes involving arbitrary changes in shape, including breakup and merging of fluid volumes. Free surfaces are described using a volume of fluid (VOF) method, in which a marker concentration field variable is set to unity within the fluid of interest and to zero outside. The free surface itself is located by steep gradients in this variable. The solution proceeds by alternate applications of Galerkin finite energy techniques to solve for mass, momentum, and energy and the VOF method to determine the new locations of free surfaces. The local mobility of the fluid depends on its viscosity, which may be entered as a function of temperature and other variables. The polymer behaves as a solid where the viscosity is very high, and the melt front within the polymer can be located by the deepest nonzero velocities. Additional flexibility is provided in FIDAP by adaptable species equations and user-defined subroutines.
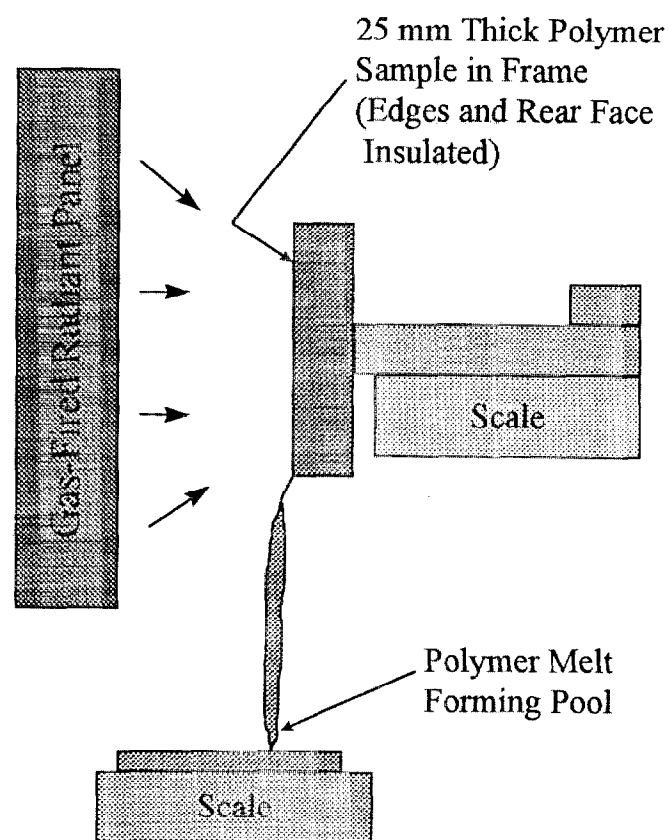
Figure 5 shows the two-dimensional input geometry for modeling the polymer melt experiment. In addition to the melting behavior of the vertically mounted polymer, the free surface capabilities of this software enable the model to consider the behavior of the melt after it has fallen away from the holder. No-slip boundary conditions are applied to the wall behind the polymer, the solid lip that holds the polymer in place, and the catch basin. The side wall is insulated, and a radiative heat flux is applied to the melt surface. Either the temperature of the catch basin or the heat flux through it is fixed. The polymer sample initially occupies a rectangular space and is assigned the appropriate material properties for polypropylene.

Both the chemical reaction responsible for polymer gasification and non-Newtonian viscosity behavior are easily included in this model. This model can also be used to investigate conditions under which the molten polymer that has dripped from the sample continues to degrade and contribute to the available fuel. The eventual extension of this model to burning polymers will be considered.

References

1) Kashiwagi, T., "Fire Safe Materials Project at NIST", Proceedings of the Fifteenth UJNR Meeting, in preparation (3/2000)

2) Zhang, J., Shields, T. and Silcock, G., *Fire and Materials* **21**, pp 1-6 (1997)

3) Kashiwagi, T., Omori, A. and Brown, J., "Effects of Material Characteristics on Flame Spreading," Fire Safety Science - Proceedings of the Second International Symposium, International Association of Fire Safety Sciences, Hemisphere Publishing, New York (1989) p. 107

Figure 1. Polymer Melt Apparatus

25 mm Thick Polymer
Sample in Frame
(Edges and Rear Face
Insulated)

Gas-Fired Radiant Panel
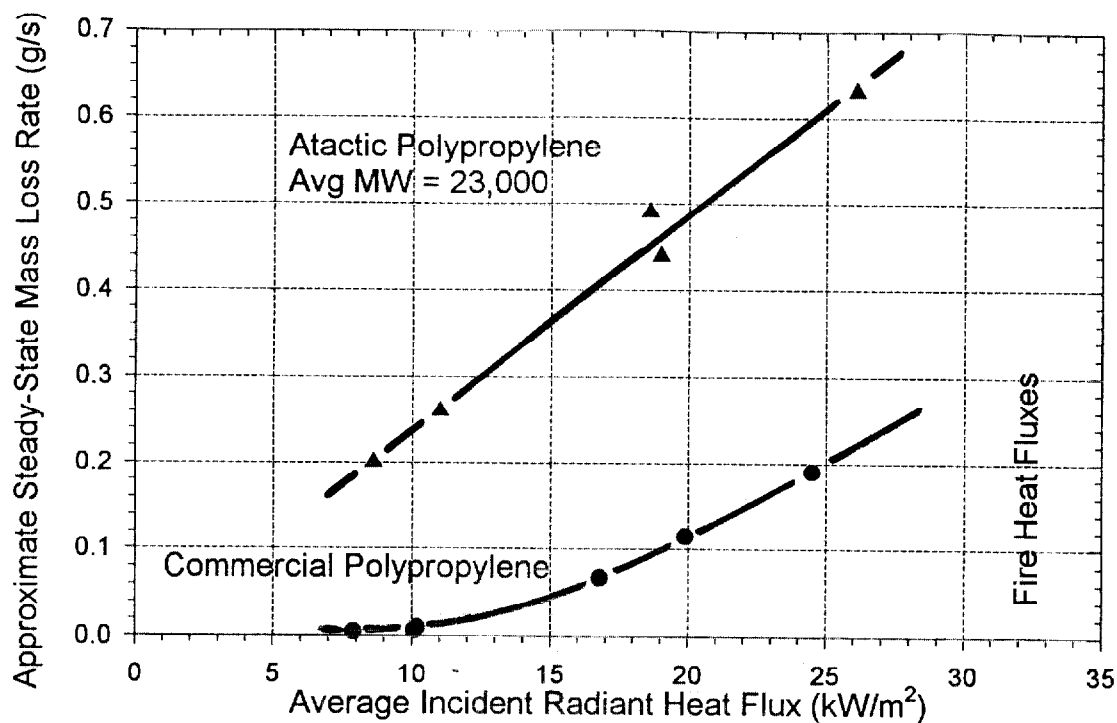
Scale

Polymer Melt
Forming Pool

Scale

Figure 2. Steady-state mass loss rate from two types of polypropylene as a function of incident radiant heat flux.
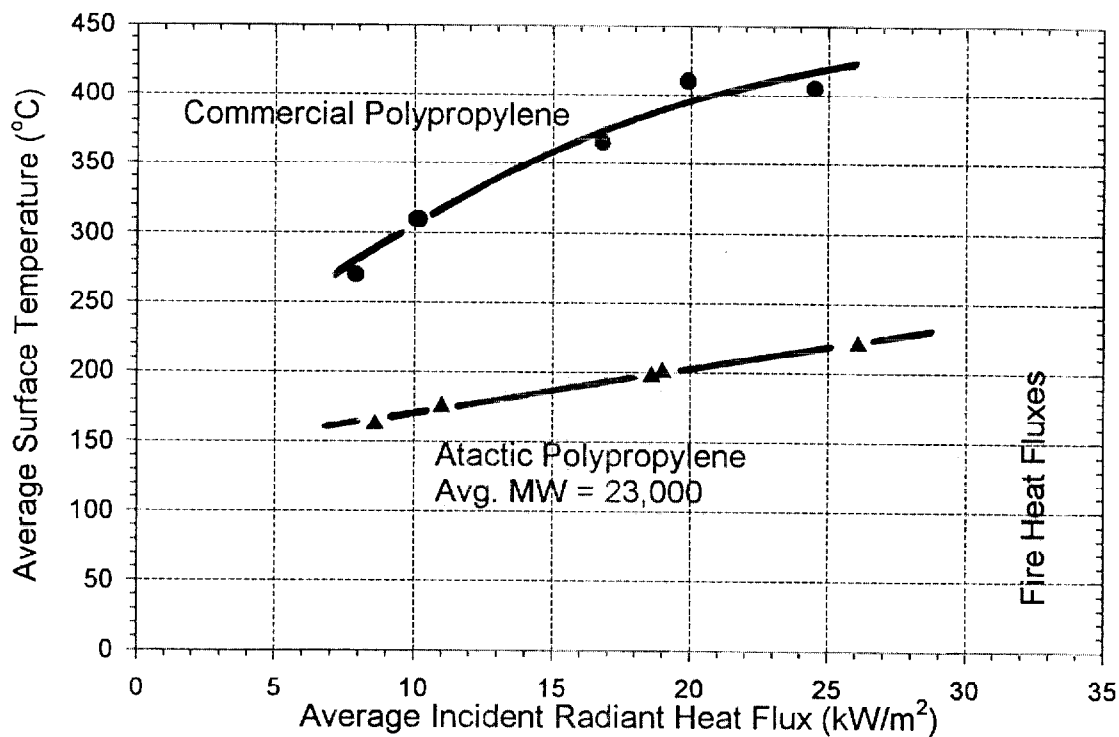

Figure 3. Average surface temperature for two types of polypropylene as a function of incident radiant heat flux.
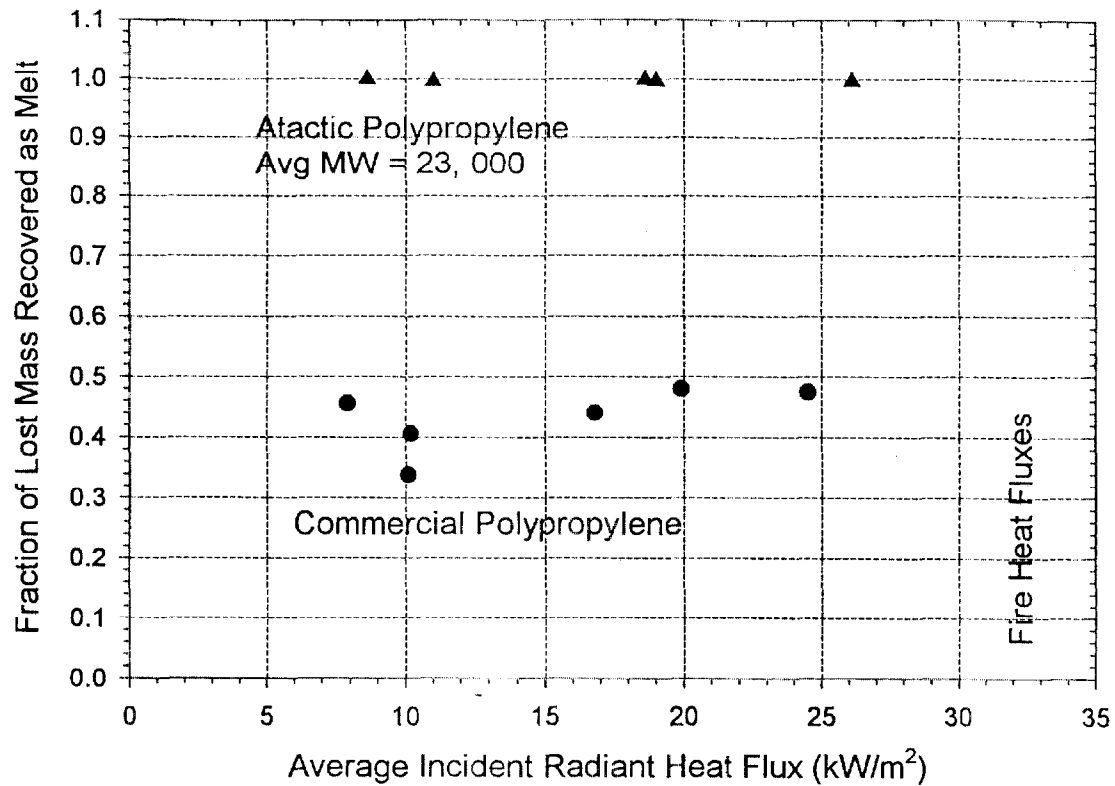
Figure 4. Fraction of mass lost from sample that is recovered in the melt pool
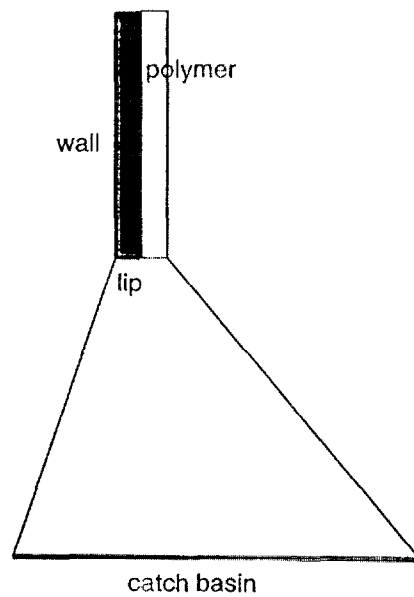for two types of polypropylene, as a function of incident radiant heat flux.

Figure 5. Computational domain for modeling the melt behavior of a
polymer heated on one exposed, vertical surface.